

# HIGHLIGHT

## Hyperbranched Polymers 10 Years After

YOUNG H. KIM

DuPont CR&D, Experimental Station, E328/261, Wilmington, Delaware 19808

Received 13 April 1998; accepted 20 April 1998



Young H. Kim

Dr. Young H. Kim obtained a BS and MS at Yonsei University, Korea, then a Ph.D. at The Weizmann Institute of Science, Israel, with Dr. E. Gil-Av in the subject of chiral recognition. After postdoctoral work with Prof. D. Cram at UCLA working on the stereoselective synthesis and cavitands, he moved to the DuPont CR&D in 1984. Since then, he has started to get involved in polymer research, and has been working on hyperbranched dendritic polymers, aromatic polyamides, and chemical modification of polymers, polyurethane chemistry.

**ABSTRACT:** It has been about 10 years since the first intentional preparation of hyperbranched polymer was disclosed. Hyperbranched polymers, as well as dendrimers, may find utilities in the areas where the structural uniqueness of these polymers gives merit. There has been much progress in the structural understanding and the methods of synthesis of these polymers. However, functional understanding and utility of these polymers are still in infancy. Better understanding on physical properties of these polymers, such as solubility and miscibility of these polymers in solvents or with polymers, and functional group dependency to the thermal relaxation process are needed for further development of the subject. © 1998 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 36: 1685–1698, 1998

**Keywords:** hyperbranched polymer; dendrimers; comb-burst dendrimers

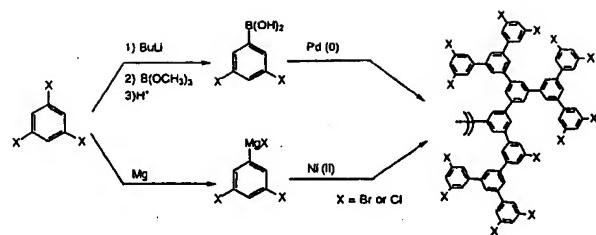
### HISTORY

In the early 1980s, a surge of enthusiasm had permeated the DuPont polymer research community with success of the group transfer polymer-

ization (GTP).<sup>1–5</sup> Room-temperature living polymerization of acrylic monomers opened a door to a variety of architectural polymers. Star-shaped polymers with a large number of active functional groups particularly attracted much attention, because thin films with these star polymers as a crosslinking agent were found to give exceptionally high toughness even at low temperature.<sup>6–9</sup>

Flexibility of the crosslinking constituents as well as the large number of functional groups can be hypothesized to account for the superior performance. This discovery triggered curiosity toward architectural polymers, in which the branching is more dense and the total number of functional groups is greater. This type of polymer was envisioned to be obtained by condensation polymerization of  $AB_x$ -type monomers, and coined internally in DuPont as "hyperbranched polymers." Polymers of such architectural characteristics had been widely considered theoretically, and have been a subject of polymer textbooks,<sup>10</sup> but intentional manifestation of hyperbranched polymers had not been demonstrated by then. While DuPont scientists were involved in construction and characterization of hyperbranched polymers, a number of scientists in various affiliations turned out to be working on similar types of compounds for different reasons, which appeared to be geared more toward the fascination of the beauty of the geometry. Research on compounds with a cascading architecture<sup>11,12</sup> or a symmetric tree branching architecture<sup>13-18</sup> provides examples. The synthetic strategies for these materials were typically aimed to produce pure macromolecular compounds. Some aimed to produce "pure" polymers with molecular weight in the range where only biological systems were able to produce. This was also the period that rich imagination not only flourished in the science but also in nomenclature of these compounds. The names termed were mostly rooted from the shapes of these compounds, which resembled the branching structure of tree. Thus, names like star-burst dendrimer<sup>13</sup> or cascade molecule arborols<sup>16</sup> were suggested. Single-step synthesis of the highly branched polymer was settled down as a hyperbranched polymer.<sup>19</sup> Second-order hyperbranched polymers, namely highly branched polymers with oligomers as the branching arm, were coined as comb-burst dendrimer,<sup>20,21</sup> or arborescent graft polymer.<sup>22</sup> Interestingly, the development of this area has coincided with public fascination of the fractal structure, and progress in the fractal theory certainly has helped in the characterization of hyperbranched polymers and in publicity.

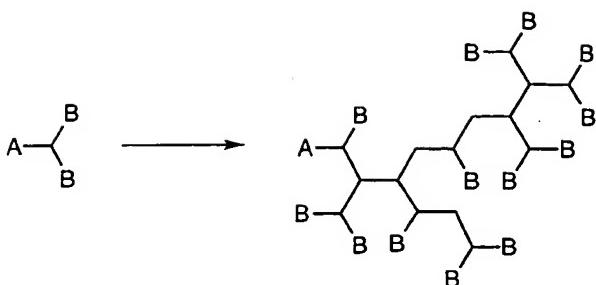
It has been just about 10 years since the first intentional preparation of hyperbranched polymer was warranted as a patent in 1987,<sup>23</sup> and public disclosure at the 1988 American Chemical Society Meeting at Los Angeles.<sup>19</sup> The first type of polymer investigated was aliphatic polyesters with hydroxy or carboxy terminal groups.<sup>24</sup> How-



Scheme 1.

ever, characterization of these polymers was found to be erratic, particularly because of irrational solubility of those polymers. The molecular weight determined by GPC was irreproducible. Polyphenylene is one of the most intractable polymers known. Hyperbranched polyphenylenes, on the other hand, exhibit excellent solubility properties. Compared to aliphatic hyperbranched polymers, rigid monomer segments offer more open and accessible cavities where solvation can be accommodated for dissolution.<sup>23</sup> Compared to linear *p*-polyphenylene, which is one of the most intractable polymers, such a high solubility of hyperbranched polyphenylenes was surprising. Highly branched polyphenylenes were synthesized from  $AB_2$ -type monomers, for example, (3,5-dibromophenyl)boronic acid and 3,5-dihalophenyl Grignard reagents as shown in Scheme 1. These monomers were polymerized by Pd(0) and Ni(II)-catalyzed aryl-aryl coupling reactions, respectively. Polymers with molecular weights 5000–35,000 and polydispersities < 1.5 were obtained, with a branching factor of about 0.8. These polymers were thermally stable to 550°C and soluble in many organic solvents, with a  $T_g$  at 236°C. The bromine functional group was converted to various groups, through lithiation or coupling reactions, to give other functional polymers with vastly different relaxation and solubility characteristics. Some of these derivatives were used as multifunctional initiators to prepare star polymers, for example, via ring-opening polymerization of propiolactone and anionic polymerization of methyl methacrylate.<sup>25</sup> Reaction of the polymer with BuLi, followed by  $\text{CO}_2$ , resulted in a water-soluble carboxylated polymeric lithium salt. This polymer showed properties resembling those of micelles, and was proposed to behave as a unimolecular micelle.<sup>26</sup> Surfactant properties were also observed in a Langmuir monolayer experiment and from its effect on  $\text{CaCO}_3$  crystal formation.<sup>27</sup>

While the architecture of dendrimers has captured synthetic chemist's hearts as soon as the



The Number of Unreacted A's: One

The Number of Unreacted B's: (Functionality - 1) X DP + 1

Scheme 2.

concept was known, it took some time for the polymer chemists to jump on the hyperbranched polymer wagon.<sup>28</sup> For most cases, hyperbranched polymers may be able to replace dendrimers in utility,<sup>29</sup> but they can be prepared much more rapidly and economically. Nevertheless, as the intensity of curiosity increases, more diverse inquiries on the subject emerged. Some of the inquiries may turn out to be rather obvious in retrospect, and some are of surprising nature. The most intense activities so far have been synthesis of varieties of hyperbranched polymers, with much of the effort from industrial settings. This review is to summarize my personal view in this new science area, where uncertainty furnishes much excitement.

## MOLECULAR ARCHITECTURE

Hyperbranched polymers exhibit much similarity with conventional linear polymers in many aspects. The preparation of these polymers was mainly conceived as an extension of well-known classes of polymers. Hyperbranched polymers are typically prepared by polymerization of  $AB_x$ -type monomers. When  $x$  is 2 or greater, polymerization of such monomers gives highly branched polymers as shown in Scheme 2, as long as A reacts only with B from another molecule.<sup>10,30</sup> Reaction between A and B from the same molecule will result in termination of polymerization by cyclization. This approach would produce highly branched polymers possessing one unreacted A "terminal" functional group and  $(x - 1)n + 1$  number of unreacted B "terminal" functional

groups, where  $n$  is the degree of the polymerization. Similarly, copolymerization of  $A_2$  and  $B_3$  or other multifunctional monomers also can give hyperbranched polymers, if the polymerization is kept below the gel point by limiting polymer conversion or by manipulation of the multifunctional monomer stoichiometry.

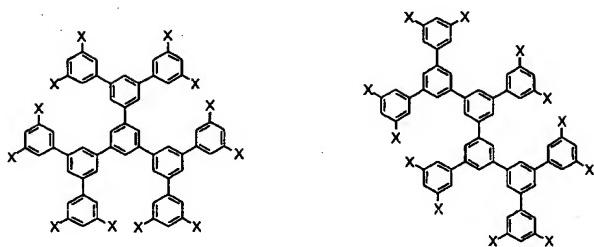
The unique properties of hyperbranched polymers are mainly manifested by their intrinsic globular structure and large number of terminal functional groups.

Unlike dendrimers, however, hyperbranched polymers have elements of conventional polymers, namely molecular weight dispersity, isomerism, and geometrical shapes. However, some new geometrically descriptive terminology has to be introduced to highlight the architectural uniqueness of these polymers. For example, the conventional polymer branching term,<sup>10</sup> the degree of branching ( $\alpha$ ) does not adequately describe the highly branched polymers. To describe the degree of perfection of the branching, a normalized branching factor was introduced.<sup>26</sup> The "branching factor,"  $f_{br}$ , is equal to the mol fraction of fully branched monomers relative to the all possible branching sites. In other words, it can be also described as the ratio between the sum of all the monomers that are fully branched and terminal vs. the total monomer units.<sup>31</sup> If we call the mol fraction of monomers at the terminal position  $T$ , unbranched linear monomer units  $L$ , and fully branched monomer units  $B$ , then,

$$f_{br} = \frac{T + B}{N_0}$$

Thus, the branching factor for a fully branched polymer, such as a dendrimer, is 1, and that of a linear isomer of high molecular weight is 0. Since  $N_0 = T + B + L$ , if one can measure the mol fraction of the  $L$  units,  $f_{br}$  can be calculated from  $1 - L/N_0$ . Thus, the degree of branching can be determined if at least one type of branched monomer units could be quantified.<sup>32</sup> The mol fractions of each type of monomer unit can be measured by a spectroscopic method, or by digestive methods.<sup>33</sup>

Isomerism is the most important distinction between hyperbranched polymers and either dendrimers or linear polymers. Because the addition of each monomer takes place randomly, a large number of geometrical isomers can be formed even for a given molecular weight and branching factor. Isomerism causes further dispersity in the



Scheme 3.

aspect ratio of the polymer molecule. Scheme 3 shows two polyphenylenes that have the same molecular weight and  $f_{br}$ , and differ in geometry. This variation of geometry has an importance on the solution as well as solid-state packing structure of the polymer and related properties. For example, the packing order influences not only the relaxation process but also affects the solubility of the polymer.

Unlike dispersity of molecular weight and branching, that of isomerism is difficult to quantify. Flory has calculated<sup>10</sup> that the number of configurations for a branched polymer is, with  $n$  equal the degree of polymerization and  $x$  is the functionality of  $B$ ,

$$\frac{nx!}{(nx - n + 1)!n!}$$

Table I shows calculated numbers of possible isomer configurations for various  $AB_x$  monomers. Obviously, the number of isomers increases with the complexity of monomers and the molecular weight of the polymers.

There have been some attempts to describe the isomeric structural characteristic designation using graph theory. Among the various topological indices, the Wiener index<sup>34</sup> seems to be useful in designating the geometry for hyperbranched polymers. Several research groups have published

mathematical logic for calculating the Wiener index<sup>35</sup> or hyper-Wiener index<sup>36</sup> for dendritic polymers. For hyperbranched polymers, a method of subgraph enumeration of orbital and wedgeal population, and its relationship with some structural properties such as molecular weight and volume, were exemplified.<sup>37</sup>

Hyperbranched polymers are closer to conventional polymers in terms of molecular weight distribution than dendrimers. Due to variations in the degree of branching, the molecular-weight distribution could be broader than that of the linear polymers. The polydispersity of the hyperbranched polymers is expected to increase to infinity at infinite polymer molecular weight. In the case of  $AB_2$  type trifunctionality monomers, one would expect a significant increase in the polydispersity when the monomer conversion reaches about 90%. The molecular weight distribution of imperfect dendrimers, which has a structure similar to hyperbranched polymers but are obtained by multistep synthesis, was found to be narrow.<sup>38</sup>

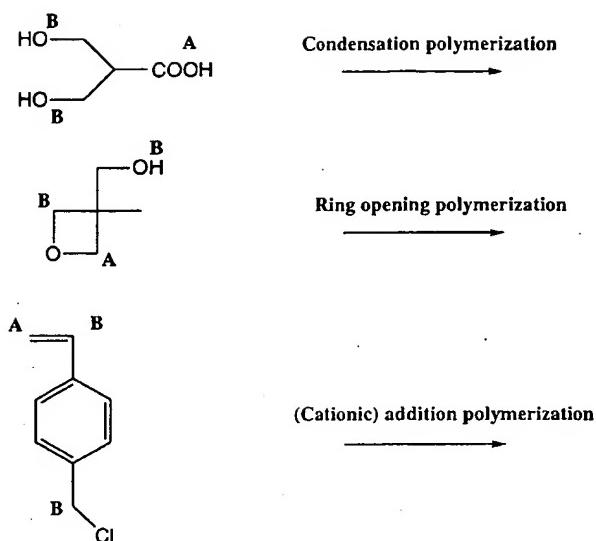
In reality, the GPC molecular-weight measurement reflects the radius of gyration of polymer due to not only its molecular weight but also the size differences due to geometrical isomerism. Even though the absolute molecular weight of hyperbranched polymers can be obtained through a universal calibration method, it may not be legitimate to define the polydispersity of hyperbranched polymers based solely on a GPC measurement.

## SYNTHESIS

In principle, practically all known polymerization methods, condensation, addition, ring opening, etc., can be employed to polymerize  $AB_x$  type monomers, as shown in Scheme 4. Solution polymerization is the most favored mode of polymer-

Table I. Number of Possible Isomers in Hyperbranched Polymers

$N_0$	Generation Number for $AB_2$ Dendrimers	Number of Configuration $\times$ in $AB_x$		
		2	3	4
4	1	1.40E+01	5.50E+01	1.40E+02
10	2	1.68E+04	1.43E+06	2.73E+07
22	3	9.15E+10	4.05E+15	4.52E+18
46	4	8.74E+24	1.09E+35	



Scheme 4.

ization, but neat polymerization,<sup>39,40</sup> solid-state-supported polymerization, etc., was also reported.<sup>41</sup> Continuous, slow addition of an  $AB_2$  monomer to a suspension of polystyrene beads functionalized with a focal-point monomer results in the simultaneous growth of hyperbranched polymers in solution and on the support. Interestingly, the polydispersity of the support-bound polymer was ca. 1.3, among the lowest yet observed for the hyperbranched polymers.

#### Condensation Polymerization

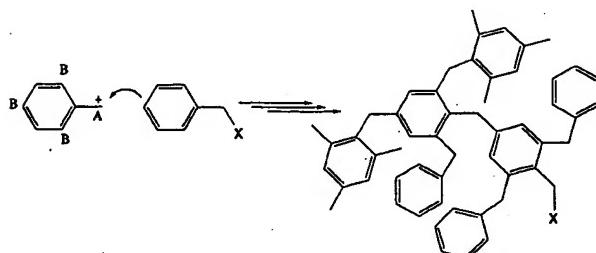
It is conceptually most obvious to identify condensation polymerization monomers that have an  $AB_x$  type structure. For this reason these monomers are the ones studied most extensively. Probably most early work on this area may not have been designed to prepare hyperbranched polymers intentionally, because unusual properties for these polymers were not appreciated then. Many classes of monomers fit into this category.

Thermoset polymers made of benzylic units have been known for a long time, for example, Bakelite. Controlled cationic polymerizations of benzylic compounds are known to produce soluble polymers, which should have a highly branched structure.<sup>42</sup> Benzyl halide or benzyl alcohol can generate a benzylic cation that will undergo condensation via aromatic electrophilic substitution either *ortho* or *para* position, leading to hyperbranched polymers (Scheme 5). Unfortunately,

most of these polymers have not been characterized extensively.

The possibility of using hydroxyl-terminated hyperbranched polymers as multifunctional crosslinking agents was recognized as early as 1972. Polymers obtained by condensation of a polyhydroxy monocarboxylic acid, such as bis(hydroxymethyl)propionic acid, were used in coating compositions.<sup>43</sup> Similarly, aliphatic hyperbranched polymers derived from higher molecular weight  $AB_x$ -type monomers, prepared by Michael addition of  $\omega$ -hydroxy amine to arylates, as well as fully aromatic polyesters (polyarylates) were reported.<sup>24</sup> Numerous methods and structure variations for hyperbranched polyarylates have appeared.<sup>31,44–50</sup> Various copolymers with  $AB$ -type monomers were also prepared. The  $T_g$ 's of the copolymers vary largely with the mole fraction of branching units and with the nature of the end groups. In the case of phenolic OH and acetate end groups, the relationship between the  $T_g$  vs. number of branching units passes through a minimum  $T_g$  around 100–120°C.<sup>51</sup> On the other hand, it was suggested that copolymerization of  $AB_2$  and  $B_3$ -type monomers, for example, dimethyl 5-(2-hydroxyethoxy)isophthalate and trimethyl 1,3,5-benzenetricarboxylate, could give better geometrical control in the hyperbranched polymer synthesis.<sup>52</sup> A monomer containing both aliphatic and aromatic reactive groups is reported to produce a hyperbranched polymer with less internal ring formation. Condensation of 4,4-(4'-hydroxyphenyl)pentanoic acid gave high molecular polymer with more than 95% of the acid functional groups remaining.<sup>53</sup>

Hyperbranched aliphatic polyesters with molecular weights in the range of 1200–44,300 were synthesized in the molten state from 2,2-bis(hydroxymethyl)propionic acid and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol as a core molecule using acid catalysis. This polymer showed a lower Mark-Houwink's "α" constant than linear poly-

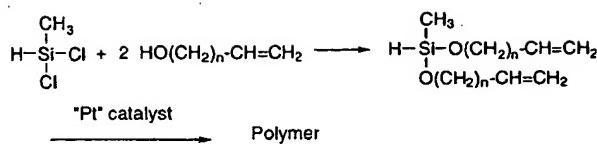


Scheme 5.

mers, but the viscosity of the solution was greatly affected by the surface functionality.<sup>54</sup> The polymerization is a pseudoone-step reaction where stoichiometric amounts corresponding to each generation were added successively.<sup>55</sup> A kinetic study of polymerization of 2,2-bis(methylol)propionic acid indicated that the reaction rates were strongly dependent on the miscibility of the monomer and the polyol core material. Trimethylolpropane (TMP) core material exhibited the highest rate of reaction, due to the low melting temperature of TMP and good solubility and mass transfer of heterophase 2,2-bis(methylol)propionic acid in the TMP melt.<sup>56</sup>

Even though some polyamide dendrimers, including polypeptide dendrimers are reported,<sup>57-59</sup> not many aliphatic polyamides have been investigated yet. In the area of aromatic polyamides, condensation of 3,5-diaminobenzoyl chloride or 3-aminoisophthalyl chloride in an amide solvent gave hyperbranched polymers. The GPC analysis of these polymers in a solvent containing a complexing salt showed that the molecular weight ranged between 24,000 and 46,000 with polydispersities of 2.0–3.2, GPC in the absence of a complexing salt indicated a high degree of polymer aggregation.<sup>60</sup>

A few hyperbranched polyether polymers are known. Most of the work in this class of polymers has been concentrated in polybenzyl ether or polyphenylene ethers. Condensation of 3,5-dihydroxy benzylbromide with  $K_2CO_3$  in the presence of a crown ether gave polyethers with various molecular weights that were solvent dependent;<sup>61</sup> 2,4,6-Tribromo phenol is an example of an  $AB_3$  type of monomer, and can be polymerized via an oxidative free radical intermediate. A low molecular weight polymer obtained with 1 equivalent of NaOH and a catalytic amount of  $K_3Fe(CN)_6$  showed a  $T_g = 148.8^\circ C$  by DSC. High molecular weight polymers can be obtained in high yield by adding KOH to neutralize the phenol, assuring thereby by complete dissolution of the phenol in



Scheme 7.

water prior to the addition of the initiator. Under standard phase-transfer catalyst conditions with tetrabutylammonium fluoride as the phase-transfer catalyst, only a low molecular-weight polymer ( $M_p = 1100$ ) was obtained.<sup>62</sup>

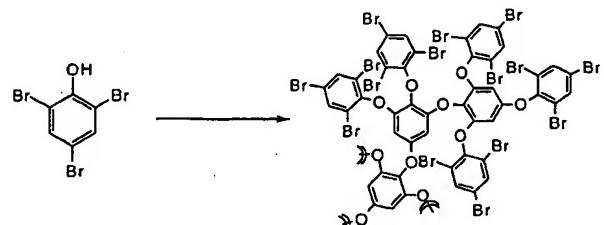
Hyperbranched structures of polymers commonly used as engineering plastic were also reported, apparently with the hope that these polymers would provide exceptional properties. These attempts have neglected the fact that a hyperbranched structure would not let the polymer molecules engage in chain entanglement, which is a necessity for the mechanical properties of the engineering plastics. Polyetherketones, both of dendrimer and hyperbranched structures,<sup>63</sup> and polyaryl ethers analogous to common linear polyaryl ethers are described along this line.<sup>64,65</sup> More recently, fairly high molecular-weight hyperbranched aromatic polycarbonates derived from 1,1,1-tris(4'-hydroxyphenyl)ethane were reported.<sup>66</sup>

Incorporation of metals or hetero atoms in dendrimers has been a popular pursuit, especially in attempts to prepare soluble polymeric catalysts. That type of efforts has not been seen much in the hyperbranched area yet. Silicon-containing polymers are the only reported hyperbranched hetero atom polymers so far. The most common polymers are hyperbranched polysiloxanes, where usually hydrosilylation to a various length of the olefinic chain was used to prepare polymers with varying degree of success.<sup>67-71</sup>

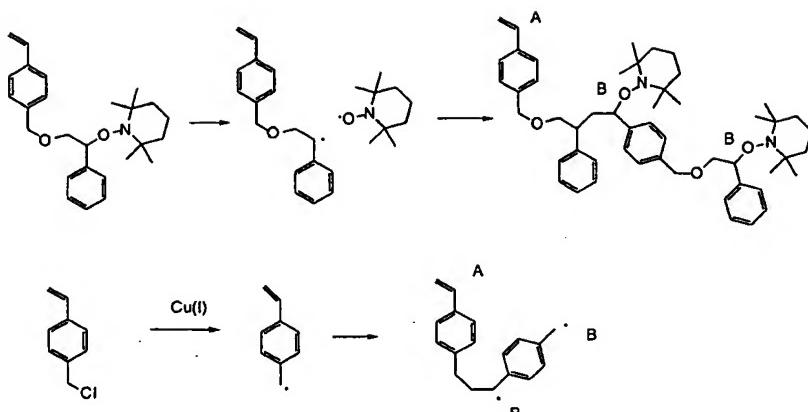
Polysilane hyperbranched polymers containing Si atoms connected to three and four other Si atoms were prepared. Copolymers made from  $RSiCl_3$  ( $R = n$ -hexyl, Ph, and Me) and  $MePhSiCl_2$  resemble hybrid materials of polysilyne and polysilanes.<sup>72</sup>

### Addition Polymerization

Addition polymerization of monomers that contain an initiating function and a propagating function in the same molecule, has been shown to give hyperbranched polymers. Unlike the  $AB_x$ -type structure required by condensation polymers, addition polymerization renders the hyper-



Scheme 6.



Scheme 8.

branched polymer by multiple reactive sites, which are generated as a result of vinyl addition reaction in addition to the already existing initiating function. A number of vinyl monomers containing a pendant group that was transformed into an initiating moiety by the action of an external stimulus were self-polymerized.

Hyperbranched polymers were prepared from 3-(1-chloroethyl)-ethyl benzene by cationic polymerization,<sup>73</sup> and from 4-[2-(phenyl)-2-(1,2,2,6,6-tetramethylpiperidinyloxy)ethoxy]methyl styrene<sup>74</sup> or *p*-(chloromethyl)styrene<sup>75</sup> by free radical polymerization. In the cationic living polymerization, the benzylic chloride of 3-(1-chloroethyl)-ethyl benzene is activated with SnCl<sub>4</sub> in the presence of Bu<sub>4</sub>NBr,<sup>76,77</sup> followed by low-temperature living cationic addition polymerization of a styrenic double bond. The Mark-Houwink  $\alpha$  constant for this series of polymers was 0.43, in contrast to 0.7 for a linear polystyrene. Recent advances in free radical living polymerization have allowed more facile preparation of hyperbranched polymers. TEMPO-assisted styrene polymerization<sup>78</sup> or Atom Transfer Radical Polymerization (ATRP)<sup>79</sup> of *p*-(chloromethyl)styrene provided hyperbranched polymers.<sup>75</sup>

Similarly, group transfer polymerization of 2-[2-methyl-1-(triethylsiloxy)-1-propenyl]oxylethyl methacrylate gave polymers with a hyperbranched-structure.<sup>80,81</sup> A method of calculation for the molecular-weight distribution (MWD) and its moments for hyperbranched polymers formed by self-condensing vinyl polymerization was reported.<sup>82</sup>

### Ring-Opening Polymerization

There are few examples of hyperbranched polymer synthesis using ring-opening polymerization.

We have attempted ring-opening polymerization of 2-hydroxyl methyl oxetane under basic conditions, which yielded only low molecular-weight polyethers.<sup>83</sup>

### Comb-Burst Dendrimers or Arborescent Graft Polymers

Another intriguing concept in building high molecular-weight highly branched polymers is that these can be prepared by grafting a polymer chain that is already grafted to other polymers. Thus, the polymer would have branches of branches, so that these polymers show no chain entanglement even at extremely high molecular weight. Tomalia has prepared such polymers in a convergent approach, and called them comb-burst dendrimers,<sup>20</sup> while Gauthier et al. have obtained structurally similar polymers and named them arborescent graft polymers.<sup>22,84,85</sup> Comb-burst polyoxazoline dendrimers were prepared by repeated sequential grafting and hydrolysis of preformed living poly(2-ethyl-2-oxazoline) oligomers on a polyethylenimine core. Arborescent graft polystyrenes were prepared by successive chloromethyl-anionic grafting sequences on polystyrene. This approach led to well-defined hyperbranched macromolecules with branching functionalities  $f > 5000$  and molar wt  $> 10^7$  g/mol, while maintaining a polydispersity below 1.3. The stiffness of the polymer chain was modulated by varying the degree of grafting sites along the chain, resulting in controllable stiffening of the molecule structure. Static and dynamic light-scattering experiments showed that the polymer behaved like hard spheres in dilute solution. Measurements in the semidilute range, however, showed a progressive

structural stiffening effect as the degree of branching increased.<sup>86-88</sup> A similar approach was used in the synthesis of hyperbranched polyisoprene.<sup>89,90</sup> These polymer shapes can be prepared if the chain termini or the chain backbone contains well-defined initiating functional groups. For example, highly branched polyethylene oxide was prepared by this method. A multifunctional initiator was used to form the first generation branched polyethylene oxide. This living polymer was end-capped with a latent multifunctional group. Upon reactivation, the chain ends provided sites for further branching.<sup>91</sup>

The most intriguing aspect of all these polymers is that their properties depend more on the chain length between the branching points than the total molecular weight. Thus, if the chain length between the branching point is less than the critical molecular weight for chain entanglement ( $M_c$ ), the polymer behaves as a low molecular-weight polymer (with the slope of a plot of  $\log \eta$  vs.  $\log$  MW to be 1) regardless of the total molecular weight. When the molecular weight between the branching points increases beyond the entanglement molecular weight the slope of a plot of  $\log \eta$  vs.  $\log$  MW becomes 3.4. In other words, if the branching length is less than the  $M_c$ , the polymer shows the characteristics of a hyperbranched polymer, and would not behave like a conventional polymer regardless of the molecular weight of the polymer.

## PHYSICAL PROPERTIES AND UTILITY

Because hyperbranched polymers cannot engage in chain entanglement to the same degree as linear polymers, their usefulness in conventional structural applications is futile. To find its applications other than in crosslinking chemistry, a better understanding of the physical properties of these polymers is necessary. A few intriguing possibilities have surfaced recently. Some polymers show colloid-like properties. The large number of terminal functional groups greatly influences the molecular relaxation processes of the polymer. Polymer miscibility and solubility are other issues that need to be addressed. The Flory-Huggins theory is based on the polymer chain cohesive interaction energy parameter. Because most of the interaction between the hyperbranched polymers resides at their chain ends, rather than the chain interaction, the conventional Flory-Huggins theory may not be able to predict the

miscibility of hyperbranched polymers. Even though a physical understanding of these types of polymers is highly desired, only limited effort has been given so far to this problem.

## Aggregation Properties

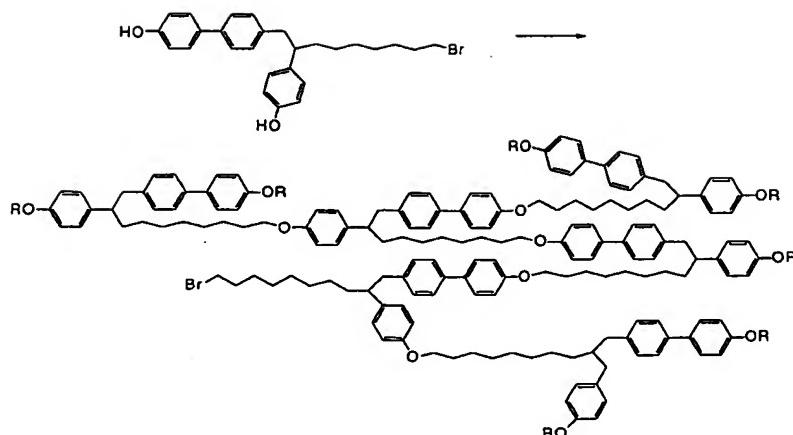
Some of these polymers exist as unusual colloid-like aggregates. Some organometallic hyperbranched polymers were found to aggregate even at a very low concentration.<sup>92</sup> A carboxylated hyperbranched polyphenylene gave oriented structure owing to partial segregation of the polymer at the air/water interface, and resulted in an usual nucleation of the  $\text{CaCO}_3$  crystal structure.<sup>93</sup>

Several hyperbranched polymers show mesophases. Thermotropic hyperbranched polymers, comprised of mesogenic branched monomer units, were described in a series of publications. Above their glass transition temperature, these hyperbranched polymers are considered to minimize their free energy by lowering their free volume via a conventional nematic mesophase, which is generated by the conformational change of their structural units from gauche to anti.<sup>94-97</sup>

On the other hand, aromatic polyamides exhibit polymer aggregation in the absence of a complexing salt resulting in a mesomorphic phase.<sup>60</sup> Similarly, a protonated hyperbranched amide with an amine center showed mesomorphism.<sup>98</sup>

## Relaxation Properties

A strong correlation between the degree of branching and the nature of the terminal groups of dendrimers and hyperbranched polymers to their glass transition temperatures has observed. The variation in the glass transition temperature as a function of molecular weight and types of chain end for dendritic polyethers and polyesters was explained with a modified chain end free-volume theory. While the modified Flory equation for  $T_g$  with consideration of the volume of end groups could explain the molecular dependence of polybenzylether dendrimer, the effect of functional groups could not be explained.<sup>99</sup> In comparing the  $T_g$ 's of hyperbranched polyphenylenes (Table II) and *p,p',p''*-trisubstituted triphenylbenzenes,  $T_g$ 's were found to increase with end-group polarity for both the polymers and the models, with an almost linear correlation between these two sets of materials.<sup>100</sup> More detailed dielectric



Scheme 9.

permittivity and loss measurement for hyperbranched polyesters of 2,2-bis(hydroxymethyl)-propionic acid showed three relaxation transitions, the glass-rubber transition and two sub-glass processes with an Arrhenius temperature dependence behavior with an activation energy of  $96 \pm 2$  kJ/mol.<sup>101</sup> The activation energies of the  $\beta$  process in the polymers increased in the order of hydroxyl, acetate, and benzoate terminal groups, indicating that the benzoate-terminated polymer is the most constrained.<sup>102</sup>

Chu and Hawker have prepared an iso-structure of AB<sub>2</sub>-type monomers, which should give polyether ketone with an identical backbone structure, but with different terminal groups. A large difference in the  $T_g$  of these two iso-structural polymers also suggests the importance of the terminal groups in the polymer properties.<sup>103</sup> In fact, it is not surprising at all that hyperbranched polymers are looked as a one-to-one block copolymer with all the monomers incorporated in the inner part of the polymer and terminal groups. Due to large differences in the polarity of the connecting groups and terminal groups, the physical properties, including the  $T_g$ , would be affected by the nature of the backbone as well as the terminal groups (Table III).

To compare the general properties of hyperbranched polymers and dendrimers, Wooley et al.

have examined a model hyperbranched polyester and the corresponding dendrimer. Polymers prepared from 3-hydroxy-5-(*tert*-butyldimethylsiloxy)-benzoic acid, as a branching point, showed that thermal properties, such as  $T_g$  and TGA, were independent of polymer architecture. However, the dendritic and hyperbranched materials demonstrated comparative solubilities that were much greater than those found for the linear polymer.<sup>104</sup> Their conclusions on the thermal properties may contradict with some other findings. For examples, the  $T_g$  of hyperbranched polypHENylenes is much lower than that of dendrimers of comparable molecular weights (Table IV). This discrepancy may have originated from the fact that the hyperbranched model compound Wooley et al. have used is a pure substance, while a real hyperbranched polymer is a mixture of millions of isomers of molecular weight and isomeric structures. This large number of isomers increases the state of entropy for the system, and is expected to lower the transition temperature as indicated by

$$T = \frac{\Delta H}{\Delta S}$$

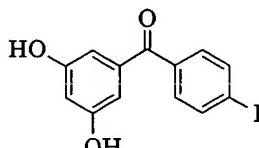
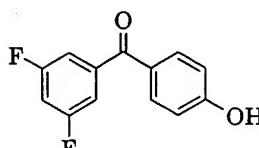
#### Applications in Crosslinking

The large number of terminal functional groups allows the use of hyperbranched polymers as mac-

Table II. The Effect of The Functional Groups on the  $T_g$  of Hyperbranched Polyphenylene

Functional Groups	Br	H	CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> Si	p-Anisol	CH <sub>2</sub> Cl	$\alpha$ -Vinyl Phenyl
$T_g$ (°C)	221	121	177	141	223	182	96

**Table III.** Properties of Iso-Structure Polyetherketone with Different Terminal Groups

Monomer	$M_n$ (D)	End Group	$T_g$	Solubility
	95000 (2.2)	OH	127	Soluble in DMF, KOH solution
	20000 (1.8)	F	162	Soluble in DMF, KOH solution

roinitiators,<sup>25</sup> or crosslinking agents. Chemically stable polymers, such as polyphenylenes, have also been used as the core of conducting star polymers. A star polymer of a hyperbranched polyphenylene core with regioregular poly(3-hexylthiophene) arms exhibits electrical and optical properties of the same or even higher structural order than the linear analogues.<sup>107</sup> A systematic investigation of hyperbranched polyesters as curing agents has been developed in Sweden. Hyperbranched aliphatic polyesters from 2,2-bis(hydroxymethyl)propionic acid and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol were used as a crosslinking agent in the coating resin formula. The resin could be UV cured, and the  $T_g$  of the hard-cured films was correlated to the difference in the structure of terminal groups in the resins.<sup>108</sup> The viscosity of alkyds based on hyperbranched polyesters and unsaturated fatty acids exhibited a substantially lower viscosity compared to similar mixtures with conventional curing agents. They also had excellent curing properties with amazingly short curing times.<sup>54,109,110</sup>

The hyperbranched polymer composite increased matrix toughness.<sup>111</sup> The size and the spherical configuration of the hyperbranched polymer eliminate the detrimental particle filtering effect observed with other conventional toughening systems. The toughness properties of both glass and carbon fiber-reinforced composites have been increased.<sup>112</sup>

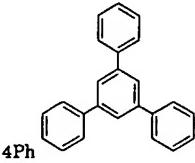
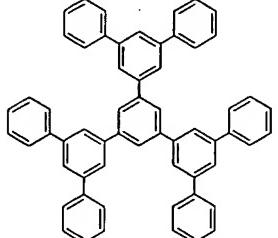
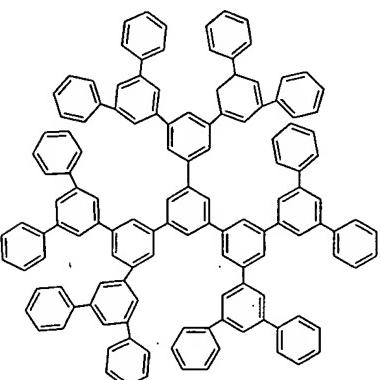
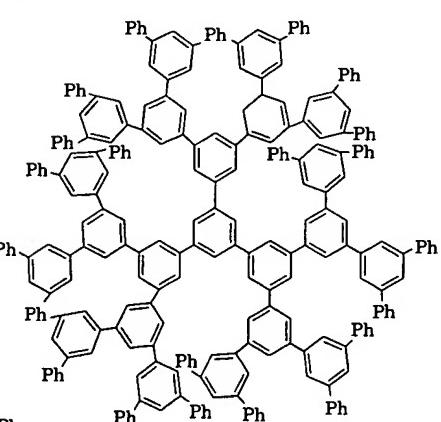
#### Polymer Solubility and Miscibility

Molecular modeling of the polymer reveals a large number of empty cavities between branches. We

speculated that a complex would form between hyperbranched polyphenylene and other aromatic groups through intercalation of the aromatic rings. Existence of such complexation was confirmed by a NMR study of carboxylated polyphenylene and *p*-toluidine.<sup>26</sup> If this interaction takes place with a polymer containing aromatic groups, it will cause a physically reversible crosslinking of the polymer chains. While PS showed reduction in the melt viscosity in the presence of brominated polyphenylene, it had no noticeable influence on the melt viscosity of PVC.<sup>25</sup> The difference between PS and PVC in rheological effect suggests that compatibility of a polymer with the hyperbranched polymer may be an important parameter for such an effect. Some of these questions have been addressed using hydroxyphenyl- and acetoxyphenyl-terminated hyperbranched polyesters. The phase behavior of blends of hydroxyphenyl- and acetoxyphenyl-terminated hyperbranched polyesters with linear polymers such as polycarbonate, polyesters, and polyamides indicated that the hydroxy-terminated hyperbranched polyester blend miscibility was identical to that of poly(vinylphenol), suggesting that strong interactions due to hydrogen bonding, more so than chain architecture, dominate the blend miscibility.<sup>113</sup>

Similar to hyperbranched polymers, arborescent polystyrene also affect the melt viscosity of linear polymers. While polymers with lower branching functionalities led to melt strengthening in the high-temperature range, the more highly branched polymers gave an almost 10-fold decreases in melt viscosity. TEM of the PMMA blends showed that melt thinning is associated

**Table IV.** The Glass and Other Thermal Transition Temperatures of Polyphenylene Dendrimers and Hyperbranched Polymers

Branched Phenylens <sup>105,106</sup>	$T_m$ (°C)	$\Delta H_f$ (kJ/mol)	$T_g$ (°C)	$\Delta C_p$ (J/°C · g)
	174.0	32.3	no Tg or 100 (?)	
	271.2	67.6	126	0.28
	338.9	74.2	190	0.22
	511.5	—	220	0.11
Hyperbranched polyphenylene with hydrogen terminal groups	None	—	121	0.26

with segregation of the branched polymer at the sample surface.<sup>114</sup>

## CONCLUSIONS

After 10 years since the introduction of hyperbranched polymer, there has been much progress in the structural understanding and the methods of synthesis of these polymers. Unfortunately, however, functional understanding and utility of these polymers are still in infancy. Due to lack of chain entanglement, these polymers do not show the properties of common polymers, such as strength and toughness, which make organic polymers so useful in the modern materials science. Hyperbranched polymers, as well as dendrimers, may find utilities in the areas where the structural uniqueness of these polymers gives merit, as we have seen the possibilities. Most likely these polymers could be useful in the area of composites, coatings, or rheology modification. However, the mechanistic understanding on the viscosity modification is poor, and there are some cases in which phase separation of the hyperbranched polymer during the crosslinking reaction caused the efficacy of these crosslinking agents to be low. At this point, there is virtually no understanding of the solubility and miscibility of these polymers in solvents or with polymer, and little effort has been devoted to obtain such an understanding. In addition, the glass transition temperature of the hyperbranched polymer depends so much on the terminal groups, and the relaxation of the hyperbranched polymer after it is incorporated in the coating is hardly understood. These would be the physical properties immediately needed to make hyperbranched polymers more widely accepted in the main stream polymer science area.

The leadership of Dr. O. W. Webster, and collaboration and discussions with Drs. G. Figuly and F. S. Fawcett was valuable for the initial stage of the program. Technical assistance of DuPont analytical staffs, and talented technicians S. Orescan and S. Baer are greatly appreciated.

## REFERENCES AND NOTES

1. O. W. Webster, U.S. Pat. 4417034 (1983).
2. O. W. Webster, W. B. Farnham, and D. Y. Sogah, EP 68887 (1983).
3. D. Y. Sogah and O. W. Webster, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 927 (1983).
4. O. W. Webster, *Science*, **251**, 887 (1991).
5. O. W. Webster, *Makromol. Chem., Macromol. Symp.*, **33**, 133 (1990).
6. J. A. Simms and H. J. Spinelli, *J. Coat. Technol.*, **59**, 125 (1987).
7. C. S. Hutchins and H. J. Spinelli, EP 258065 (1988).
8. P. Lang, H. J. Spinelli, L. Page, M. S. Wolfe, and W. Burchard, *Macromolecules*, **24**, 1306 (1991).
9. H. J. Spinelli, *Methacrylate Star Polymers via Group-Transfer Polymerization*, H. J. Spinelli, Ed., Springer, Berlin, 1991, p. 249.
10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
11. E. Buhleier, W. Wehner, and F. Voegtle, *Synthesis*, **155** (1978).
12. R. Moor and F. Voegtle, *Chem. Ber.*, **126**, 2133 (1993).
13. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, and P. Smith, *Polym. J. (Tokyo)*, **17**, 117 (1985).
14. D. A. Tomalia and J. R. Dewald, U.S. Pat. 4587329 (1986).
15. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, and P. Smith, *Macromolecules*, **19**, 2466 (1986).
16. G. R. Newkome, Z. Yao, G. R. Baker, and V. K. Gupta, *J. Org. Chem.*, **50**, 2003 (1985).
17. G. R. Newkome, G. R. Baker, M. J. Saunders, P. S. Russo, V. K. Gupta, Z. Q. Yao, J. E. Miller, and K. Bouillion, *J. Chem. Soc., Chem. Commun.*, **752** (1986).
18. G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, P. S. Russo, and M. J. Saunders, *J. Am. Chem. Soc.*, **108**, 849 (1986).
19. Y. H. Kim and O. W. Webster, *Polym. Prepr.*, **29**, 310 (1988).
20. D. A. Tomalia, D. M. Hedstrand, and M. S. Ferritto, *Macromolecules*, **24**, 1435 (1991).
21. D. A. Tomalia, D. R. Swanson, and D. M. Hedstrand, *Polym. Prepr.*, **33**, 180 (1992).
22. M. Gauthier and M. Möller, *Macromolecules*, **24**, 4548 (1991).
23. Y. H. Kim, U.S. Pat. 4857630 (1987).
24. G. D. Figuly, U.S. Pat. 5136014 (1992).
25. Y. H. Kim and O. W. Webster, *Macromolecules*, **25**, 5561 (1992).
26. Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.*, **112**, 4592 (1990).
27. J. M. Didymus, P. Oliver, S. Mann, A. Devries, P. Hauschka, and P. Westbroek, *J. Chem. Soc. Faraday Trans.*, **89**, 2891 (1993).
28. The number of publications on this subject has increased from 1–2 per year during 1987–1991 to 170 in 1997.

29. L. Hobson, *J. Chem. Commun. (Cambridge)*, 2067 (1997).
30. P. J. Flory, *J. Am. Chem. Soc.*, **74**, 2718 (1952).
31. C. J. Hawker, R. Lee, and J. M. J. Frechet, *J. Am. Chem. Soc.*, **113**, 4583 (1991).
32. Y. H. Kim, *Macromol. Symp.*, **77**, 21 (1994).
33. P. Kambouris and C. J. Hawker, *J. Chem. Soc., Perkin Trans.*, **1**, 2717 (1993).
34. H. Wiener, *J. Am. Chem. Soc.*, **17** (1947).
35. I. Gutman, Y.-N. Yeh, S.-L. Lee, and J.-C. Chen, *Match*, **30**, 103 (1994).
36. M. V. Diudea and B. Parv, *J. Chem. Inf. Comput. Sci.*, **35**, 1015 (1995).
37. M. V. Diudea, *Match*, **30**, 79 (1994).
38. M. L. Mansfield, *Macromolecules*, **26**, 3811 (1993).
39. A. Kumar and S. Ramakrishnan, *J. Chem. Soc., Chem. Commun.*, 1453 (1993).
40. A. Kumar and S. Ramakrishnan, *Synthesis and Characterization of Hyperbranched Poly(ether-ester)s with Functional Spacers*, Vol. 1, A. Kumar, S. Ramakrishnan, Ed., Allied Publ., New Delhi, India, 1994, p. 266.
41. P. Bharathi and J. S. Moore, *J. Am. Chem. Soc.*, **119**, 3391 (1997).
42. A. A. Vansheidt, E. P. Mellnikova, and G. A. Gladkovskii, *Vysokomolekul Soedin.*, **4**, 1303 (1962).
43. A. S. Baker and D. J. Walbridge, U.S. Pat. 3669939 (1972).
44. H. R. Kricheldorf, Q.-Z. Zang, and G. Schwarz, *Polymer*, **23**, 1821 (1982).
45. J. M. J. Frechet, C. J. Hawker, and K. Uhrich, WO 9208749 (1992).
46. K. L. Wooley, C. J. Hawker, R. Lee, and J. M. J. Frechet, *Polym. J.*, **26**, 187 (1994).
47. S. R. Turner, B. I. Voit, and T. H. Mourey, *Macromolecules*, **26**, 4617 (1993).
48. S. R. Turner, F. Walter, B. I. Voit, and T. H. Mourey, *Macromolecules*, **27**, 1611 (1994).
49. H. R. Kricheldorf and O. Stoeber, *Macromol. Rapid Commun.*, **15**, 87 (1994).
50. H. R. Kricheldorf, O. Stoeber, and D. Luebers, *Macromolecules*, **28**, 2118 (1995).
51. H. R. Kricheldorf, O. Stoeber, and D. Lubbers, *Macromol. Chem. Phys.*, **196**, 3549 (1995).
52. W. J. Feast and N. M. Stainton, *J. Mater. Chem.*, **5**, 405 (1995).
53. F. Chu, C. J. Hawker, P. J. Pomery, and D. J. T. Hill, *J. Polym. Sci., Part A: Polym. Chem.*, **35**, 1627 (1997).
54. A. Hult, M. Johansson, and E. Malmstroem, *Macromol. Symp.*, **98**, 1159 (1995).
55. E. Malmstroem, M. Johansson, and A. Hult, *Macromolecules*, **28**, 1698 (1995).
56. E. Malmstroem and A. Hult, *Macromolecules*, **29**, 1222 (1996).
57. C. Rao and J. P. Tam, *J. Am. Chem. Soc.*, **116**, 6975 (1994).
58. J. P. Tam and F. P. Zavala, WO 9011778 (1990).
59. R. G. Denkewalter, J. Kolc, and W. J. Lukasavage, U.S. Pat. 4289872 (1981).
60. Y. H. Kim, *J. Am. Chem. Soc.*, **114**, 4947 (1992).
61. K. E. Uhrich, C. J. Hawker, J. M. J. Frechet, and S. R. Turner, *Polym. Mater. Sci. Eng.*, **64**, 237 (1991).
62. Y. H. Kim, *Highly Branched Aromatic Polymers*, Vol. 2, Y. H. Kim, Ed., JAI Press Inc., Hampton-hill, Middlesex, 1995, p. 123.
63. A. Morikawa, M. Kakimoto, and Y. Imai, *Macromolecules*, **26**, 6324 (1993).
64. T. M. Miller, T. X. Neenan, and E. W. Kwock, *Macromol. Symp.*, **77**, 35 (1994).
65. T. M. Miller, T. X. Neenan, E. W. Kwock, and S. M. Stein, *J. Am. Chem. Soc.*, **115**, 356 (1993).
66. D. H. Bolton and K. L. Wooley, *Macromolecules*, **30**, 1890 (1997).
67. L. J. Mathias and T. W. Carothers, *J. Am. Chem. Soc.*, **113**, 4043 (1991).
68. L. J. Mathias and T. W. Carothers, *Silicon-Based Stars, Dendrimers, and Hyperbranched Polymers*, Vol. 2, L. J. Mathias, T. W. Carothers, Ed., JAI, Hampton Hill, Middlesex, 1995, p. 101.
69. A. M. Muzaferov, O. B. Gorbatshevich, E. A. Rebrov, G. M. Ignat'eva, T. B. Chenskaya, V. D. Myakushev, A. F. Bulkin, and V. S. Papkov, *Vysokomol. Soedin., Ser. A Ser. B*, **35**, 1867 (1993).
70. S. Rubinsztajn, *J. Inorg. Organomet. Polym.*, **4**, 61 (1994).
71. A. M. Muzaferov, M. Golly, and M. Moeller, *Macromolecules*, **28**, 8444 (1995).
72. J. Maxka, J. Chrusciel, M. Sasaki, and M. Krzysztof, *Macromol. Symp.*, **77**, 79 (1994).
73. J. M. J. Frechet, M. Henmi, I. Gitsov, S. Aoshima, M. R. Leduc, and B. Rubbs, *Science*, **269**, 1080 (1995).
74. C. J. Hawker, J. M. J. Frechet, R. B. Grubbs, and J. Dao, *J. Am. Chem. Soc.*, **117**, 10763 (1995).
75. S. G. Gaynor, S. Edelman, and K. Matyjaszewski, *Macromolecules*, **29**, 1979 (1996).
76. Y. Ishihama, M. Sawamoto, and T. Higashimura, *Macromolecules*, **26**, 744 (1993).
77. Y. Ishihama, M. Sawamoto, and T. Higashimura, *Polym. Bull.*, **361**, (1990).
78. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, and G. K. Hamer, *Macromolecules*, **26**, 2987 (1993).
79. J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 5614 (1995).
80. K. Sakamoto, T. Aimiya, and M. Kira, *Chem. Lett.*, 1245 (1997).
81. P. F. W. Simon, W. Radke, and A. H. E. Muller, *Macromol. Rapid Commun.*, **18**, 865 (1997).
82. H. Zhang and E. Ruckenstein, *Polym. Bull.*, **39**, 399 (1997).
83. Y. H. Kim, Unpublished results.
84. M. Gauthier, M. Moeller, and W. Burchard, *Polym. Prepr.*, **34**, 60 (1993).
85. M. Gauthier, L. Tichagwa, J. S. Downey, and S. Gao, *Macromolecules*, **29**, 519 (1996).

86. M. Gauthier, M. Moeller, and W. Burchard, *Macromol. Symp.*, **77**, 43 (1994).
87. M. Gauthier, W. Li, and L. Tichagwa, *Polymer*, **38**, 6363 (1997).
88. M. Gauthier, R. S. Frank, and G. Merkle, *Polym. Mater. Sci. Eng.*, **77**, 114 (1997).
89. R. A. Kee and M. Gauthier, *Polym. Mater. Sci. Eng.*, **73**, 335 (1995).
90. R. A. Kee and M. Gauthier, *Polym. Mater. Sci. Eng.*, **77**, 176 (1997).
91. S. Jean-Luc and Y. Gnanou, *Macromol. Symp.*, **95**, 137 (1995).
92. S. Campagna, A. Giannetto, S. Serroni, G. Denti, S. Trusso, F. Mallamace, and N. Micali, *J. Am. Chem. Soc.*, **117**, 1754 (1995).
93. J. M. Didymus, P. Oliver, S. Mann, A. L. DeVries, P. V. Hauschka, and P. Westbroek, *J. Chem. Soc., Faraday Trans.*, **89**, 2891 (1993).
94. V. Percec and M. Kawasumi, *Macromolecules*, **25**, 3843 (1992).
95. V. Percec, P. Chu, and M. Kawasumi, *Macromolecules*, **27**, 4441 (1994).
96. F.-L. Chen, A. M. Jamieson, M. Kawasumi, and V. Percec, *J. Polym. Sci., Part B: Polym. Phys.*, **33**, 1213 (1995).
97. V. Percec, P. Chu, G. Ungar, and J. Zhou, *J. Am. Chem. Soc.*, **117**, 11441 (1995).
98. U. Stebani and G. Lattermann, *Adv. Mater.*, **7**, 578 (1995).
99. K. L. Wooley, C. J. Hawker, J. M. Pochan, and J. M. J. Fréchet, *Macromolecules*, **26**, 1514 (1993).
100. Y. H. Kim and R. Beckerbauer, *Macromolecules*, **27**, 1968 (1994).
101. E. Malmstrom, F. Liu, R. H. Boyd, A. Hult, and U. W. Gedde, *Polym. Bull.*, **32**, 679 (1994).
102. E. Malmstrom, A. Hult, U. W. Gedde, F. Liu, and R. H. Boyd, *Polymer*, **38**, 4873 (1997).
103. F. Chu and C. J. Hawker, *Polym. Bull.*, **30**, 265 (1993).
104. K. L. Wooley, J. M. J. Fréchet, and C. J. Hawker, *Polymer*, **35**, 4489 (1994).
105. T. M. Miller, T. X. Neenan, R. Zayas, and H. E. Bair, *J. Am. Chem. Soc.*, **114**, 1018 (1992).
106. T. M. Miller and T. X. Neenan, *Chem. Mater.*, **2**, 346 (1990).
107. F. Wang, R. D. Rauh, and T. L. Rose, *J. Am. Chem. Soc.*, **119**, 11106 (1997).
108. M. Johansson and A. Hult, *J. Coat. Technol.*, **67**, 35 (1995).
109. B. Pettersson, *Proc. Water-Borne, Higher-Solids, Powder Coat. Symp.*, **21**, 753 (1994).
110. A. Hult, E. Malmstroem, and M. Johansson, *Polym. Mater. Sci. Eng.*, **72**, 528 (1995).
111. J. L. Hedrick, C. J. Hawker, R. D. Miller, R. Twieg, S. A. Srinivasan, and M. Trollsas, *Macromolecules*, **30**, 7607 (1997).
112. L. Boogh, B. Pettersson, P. Kaiser, and J.-A. Manson, *SAMPE J.*, **33**, 45 (1997).
113. D. J. Massa, K. A. Shriner, S. R. Turner, and B. I. Voit, *Macromolecules*, **28**, 3214 (1995).
114. A. Khadir and M. Gauthier, *Annu. Tech. Conf. Soc. Plast. Eng.*, **55**, 3732 (1997).